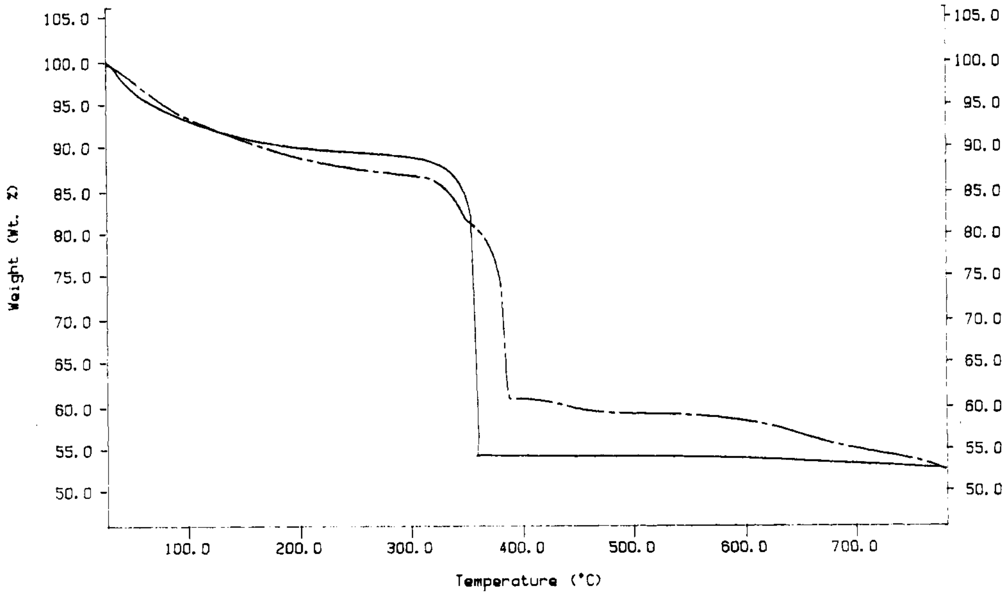

Figure 1. TGA data for the solid hydrolysis product of the reaction between $Ba(O_2CCMe_2OH)_2$ and $Ti(O\text{-}i\text{-}Pr)_4$ in pyridine showing the effects of heating in air (dashed line) versus O_2 (continuous line) atmospheres.

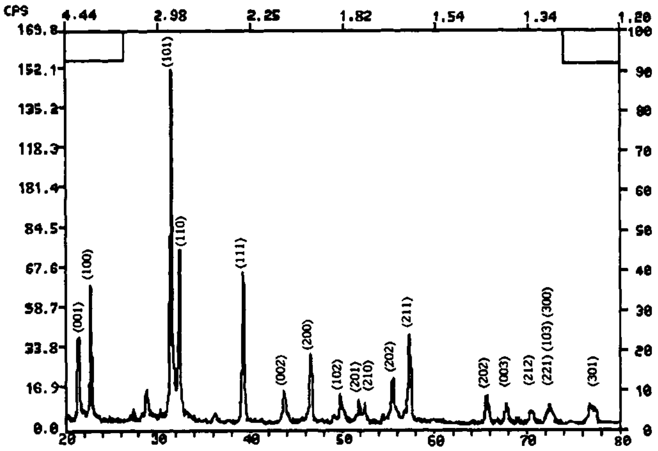

Figure 2. X-ray powder diffraction data for the $PbTiO_3$ formed from the reaction of $Pb(O_2CCMe_2OH)_2$ and $Ti(O\text{-}i\text{-}Pr)_4$ in pyridine followed by hydrolysis, removal of the volatile components in vacuo and thermolysis of the powder obtained at 350 °C in O_2. Peaks at 29° and 36° are due to the presence of a PbO impurity.

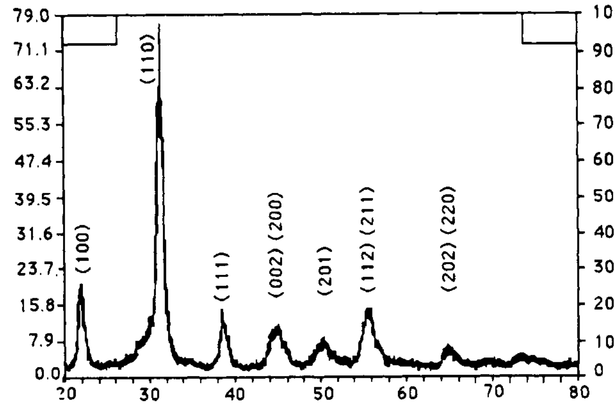

Figure 3. X-ray powder diffraction data for $PbZr_{0.52}Ti_{0.48}O_3$, see text for details.

strategy illustrated in Scheme I is successful for the formation of crystalline, complex integral and nonintegral metal oxides at relatively low temperatures and short reaction times. We are currently investigating the formation of thin films materials via this approach and the generality of these reactions to prepare other complex metal oxides.

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Registry No. $PbTiO_3$, 12060-00-3; $PbZrO_3$, 12060-01-4; $BaTiO_3$, 12047-27-7; $CaTiO_3$, 12049-50-2; $BaSnO_3$, 12009-18-6; lead titanium zirconium oxide, 106496-80-4; barium strontium titanium oxide, 116812-42-1.

Polymer Precursor Route to TiB_2/TiN Nanocomposites

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Because of their high melting points, hardness, and chemical resistance at high temperatures, metal borides and metal nitrides are two of the most important families of engineering ceramics.[3,4] We report in this communi-

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cation a polymer-based synthetic route by which monolithic nanophase titanium boride/titanium nitride composite materials may be produced in both high ceramic and high chemical yields by polymer pyrolysis under inert atmosphere.

We have previously reported the preparation of the new boron–nitrogen polymer polyborazylene, $(B_3N_3H_4)_x$, and shown that this processable polymer can be converted to boron nitride in high ceramic and chemical yields (90–94%).[5] We have also demonstrated a new, potentially general route to metal borides, such as TiB_2 and ZrB_2, involving the reduction of the corresponding metal oxide with a boron–carbon-based polymer $(B_{10}H_{12}\text{-dinitrile})_x$.[6] Work by Seyferth[7] and Greil[8] has likewise shown that pyrolysis of preceramic–polymer/metal–powder mixtures can be used to generate composite ceramics containing metal silicides, carbides, nitrides, or borides. Taken together these results suggested that the reactions of a metal with polyborazylene might lead to incorporation of both polymer boron and nitrogen atoms to produce new composite metal–nitride/metal–boride materials which might have improved properties over an individual metal boride or nitride.[9] Furthermore, since high ceramic and chemical yields should be possible with the polyborazylene/metal system without employing a reactive pyrolysis atmosphere (e.g., ammonia), then the formation of monolithic ceramic materials should be enabled.

Such a titanium boride/titanium nitride precursor system was made by dispersing titanium powder into polyborazylene. Final ceramic materials were prepared by pyrolysis of either powders or shaped green bodies under inert atmosphere:

$$(B_3N_3H_4)_x + Ti \xrightarrow{\Delta} TiN/TiB_2 + H_2$$

In a typical process, 12.1 g of titanium metal (325 mesh, Strem Chemicals) was added to a dry tetrahydrofuran solution containing 5.0 g of polyborazylene. The solvent was then vacuum evaporated while maintaining ultrasonic agitation. The resulting black solid dispersion was ground into a fine powder. A 0.78-g sample was then heated under argon at 1450 °C for 10 h, resulting in the formation of 0.69 g of ceramic material, which corresponds to 91.8% ceramic and 88.5% chemical yields. Elemental analysis of the ceramic corresponds to a composition of $Ti_{1.0}B_{0.50}N_{0.57}H_{<0.06}O_{0.1}C_{0.14}$ consistent with a $(TiN)_{0.57}(TiB_2)_{0.25}Ti_{0.18}O_{0.1}C_{0.14}$ mixture.[10,11]

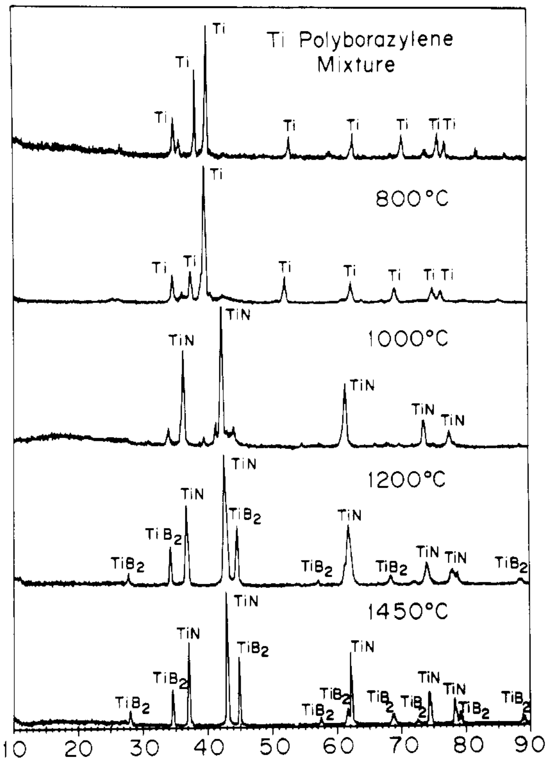

Figure 1. XRD spectra of the initial polymer/titanium powdered dispersion and bodies treated[12] at 800, 1000, 1200, and 1450 °C.

Green bodies were made by isostatic pressing of 1–5-g samples of polymer/titanium dispersions at room temperature at 75000 psi. The green bodies were then heated[12] under argon separately at 1000, 1200, and 1450 °C, resulting in the production of ceramic bodies with ceramic yields of 96.0%, 95.5%, and 94.9%, respectively. The final ceramic bars showed excellent shape retention. The ceramic monolith prepared at 1000 °C had a linear shrinkage of about 6%. The densities of the ceramic bodies increased from 3.0 (1000 °C) to 3.9 (1450 °C) with the increasing reaction temperatures.

A TGA study of the ceramic conversion reaction showed weight losses in the ranges 50–300 and 450–800 °C, similar to those observed in the conversion of pure polyborazylene to boron nitride.[5] At 1350 °C an additional weight loss was observed which, consistent with an observed decrease in the oxygen content of materials treated above this temperature,[10] is probably due to evaporation of B_2O_3 produced by the reduction of titanium oxide impurities by boron.

X-ray diffraction studies of the ceramic conversion reaction have shown that the product exhibits variations in composition and crystallinity as the processing temperature and/or time is increased. Thus, as can be seen in Figure 1, there appears to be little reaction between the polymer and the titanium metal when the sample was heated at 800 °C for 9.5 h. Consistent with this conclusion, elemental analyses of a sample at this point showed that the material still had a significant hydrogen content[10] with the observed $B_{1.03}$:$N_{1.0}$:$H_{0.79}$ ratio suggesting that polymer cross-linking was still occurring. When the sample was heated at 1000 °C for 2 h, the titanium metal was completely consumed by reaction with the polymer and crystalline titanium nitride was initially observed to form. The

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(10) Elemental analyses: 1450 °C ceramic: Ti, 73.4%; B, 8.31%; N, 12.2%; O, 2.91%; C, 2.66%; H, < 0.1%; 800 °C material: Ti, 65.8%; B, 9.80%; N, 12.3%; O, 8.58%; C, 0.66%; H, 0.70%. All analyses were performed at Pascher, Remagen, Germany.

(11) Carbon impurities may have come from the carbon crucibles used for pyrolysis.

(12) The green bodies were first annealed at 800 °C for 9.5 h, then heated (5 °C/min) separately to 1000, 1200, or 1450 °C and held at temperature for 2 h.

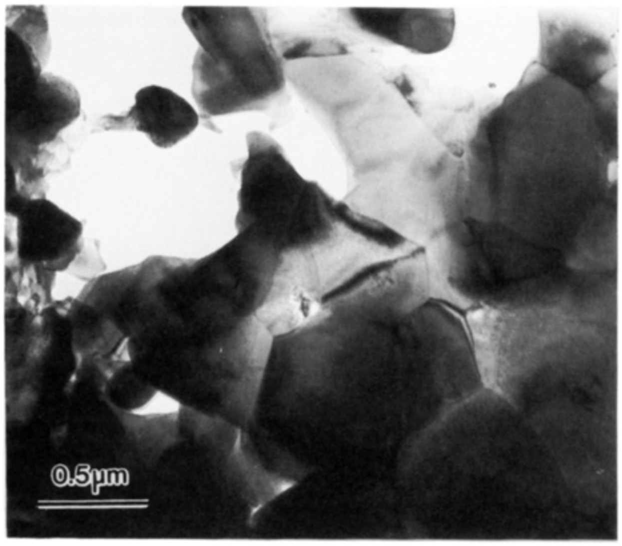

Figure 2. TEM of ceramic body treated at 1450 °C.

formation of crystalline TiB_2 was observed only upon heating of samples for either longer times (1000 °C, 3 days) or at higher temperatures (1200 °C, 1 h). The spectrum shown in the figure obtained from the sample annealed at 1200 °C for 2 h clearly indicates the presence of both crystalline TiB_2 and TiN. The decrease in the linewidths in the spectrum of the 1450 °C sample is consistent with an increase in the average crystal size.[13] SEM studies of bodies prepared at 800, 1000, 1200, and 1450 °C also indicate a change in morphology after 1000 °C suggesting the onset of reaction.

Consistent with the above results, TEM analysis of the compact annealed at 800 °C for 9.5 h shows the presence of 20–100-nm spherical crystals embedded in an amorphous matrix. These crystals could be either unreacted titanium metal or nucleated titanium nitride. For the ceramic compact annealed at 1200 °C,[12] TEM shows angular grains on the order of 50–100 nm which have two contrast levels. While it is tempting to assign these contrast levels to the two phases detected by X-ray diffraction, electron diffraction was impossible due to the size of the crystals. In agreement with the XRD study, the TEM of the 1450 °C sample presented in Figure 2, shows that two types of grains are still evident but that they have increased in size. There is some indication of a residual amorphous phase in both the images and electron diffraction patterns.

The preparations of TiB_2/TiN and TiB_2/Ti(CN) composite materials by sintering TiB_2 and TiN or TiCN powders at high temperatures have previously been reported.[14] Seyferth has also reported that a crystalline TiB_2/TiN powder composite can be made by the pyrolysis of $[B_{10}H_{12}\text{-diamine}]_x$ polymer/Ti under NH_3 atmosphere.[7] TiB_2/TiN composite coatings have also been achieved by CVD methods.[15] The polyborazylene-based route discussed herein is unique, however, in that it is the only reported direct chemical method which can be used to produce monolithic titanium boride/nitride composites, consisting of intimately mixed polycrystals with grain sizes on the order of nanometers, in high ceramic and chemical yields. The dependence of the crystal size and its distribution on the reaction/sinter temperature, the evolution of microstructure and the properties of the final composite material, such as conductivity and hardness are currently under investigation. We are also exploring the reactions of polyborazylene with other metals and soluble metal complexes with the goal of developing a range of new metal boride/nitride precursor systems that will allow the formation of both shaped bodies and coatings.

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Registry No. Ti, 7440-32-6; TiN, 25583-20-4; TiB_2, 12045-63-5; polyborazylene, 143186-38-3.

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Stable Second-Order Nonlinear Optical Polyimide/Inorganic Composite

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The second-order nonlinear optical (NLO) properties of polymeric materials have been attracting a lot of attention,[1–15] especially for such potential applications as fast waveguide electrooptic modulation and frequency-doubling devices. The ultimate applicability of polymeric materials for second-order nonlinear optics may depend upon the ability to produce polymers whose orientation has sufficient stability for incorporation into practical devices.[4] To

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